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(54) **Process for producing isobutene**

(57) Process for producing isobutene which process comprises contacting a propylene containing feed with a catalyst consisting of a crystalline silica polymorph of the silicalite type, in the presence of steam, the molar ratio of water: feed being from 0.5 to 5:1.

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## SPECIFICATION

## Process for producing isobutene

- 5 The present invention relates to a process for selectively producing isobutene from propylene or from a mixture of hydrocarbons containing propylene. 5
- Measures which have been adopted to ban the use of tetraethyllead in motor-fuel have lead the petrol industry to study other additives, including oxygen containing additives, which improve the octane number of motor-fuel. Among these additives, asymmetric ethers, and more particularly methyl tert-butyl ether (MTBE), have proved to be very efficient. MTBE is prepared from ethanol and isobutene. 10
- Isobutene is also used as a starting material for the production of other valuable compounds, such as t-butyl alcohol (used as solvent), t-butyl phenol (used as stabilizer), low molecular weight polymers (used to improve the viscosity index of lubricating oils), etc. However, the present capacity for producing isobutene does not provide sufficient amounts of these derivatives to satisfy their potential market. 15
- There is accordingly a need for a process for producing simple and economically isobutene starting from other starting materials than those presently used.
- A surplus of propylene or of propylene containing fractions is available from oil refineries. It has already been proposed to upgrade feeds containing normally gaseous olefins by an oligomerisation reaction in at least two steps leading to the formation of normally liquid olefinic products. 20
- U.S. Patent 4,414,423 to S. J. Miller discloses a method for upgrading feeds containing normally gaseous olefins by an oligomerisation reaction in at least two steps leading to the formation of high boiling point hydrocarbons. This method may be applied to propylene or to a mixture of propane and propylene as starting materials. Normally liquid olefins are formed by oligomerisation in a first step, and they are converted into higher oligomers in a second step. The object of the method described in this patent is to give good yields of high boiling point hydrocarbons. During the first step, a minimal amount of C<sub>4</sub> olefins (of which isobutene is only one of the three isomers) is formed starting from a mixture of propane and propylene. Such a method can therefore not be used for the selective production of isobutene from propylene or from a gaseous feed which contains propylene. 25 30
- The present invention aims to provide an economical process for selectively transforming propylene into isobutene.
- 35 According to the present invention there is provided a process for producing isobutene which process comprises containing a propylene containing feed with a catalyst consisting of crystalline silica polymorph of the silicalite type, in the presence of steam, the molar ratio of water:feed being from 0.5 to 5. 35
- The starting feedstock for the process of the present invention may be either essentially pure propylene or fractions obtained during the refining process and which may contain as little as 10 vol % of propylene. Said fractions may contain other low molecular weight olefinic hydrocarbons, as well as saturated hydrocarbons having from 1 to 4 carbon atoms, including propane which is also partially converted by the process of the present invention. 40
- The catalyst is a crystalline silica, polymorph and unmodified, of the silicalite type. Therefore it is a substantially pure silica, which means that it does not contain either impurities or modifying elements or that it only contains traces of them. The preparation method and the structure of the silicalite are described in U.S. Patent 4,061,724 by Grose, incorporated herein by reference. 45
- The propylene containing feed is contacted with silicalite in the presence of steam. It has indeed been unexpectedly found that the presence of water not only improves the life of the catalyst, but also, and more important, promotes the production of butenes, and in particular of isobutene, by reducing the formation of heavier products. Owing to the presence of steam, the isobutene selectivity is increased by about 50%, all other factors being equal. The term "isobutene selectivity" means the weight of isobutene formed, calculated on 100 parts by weight of converted feed. At the lower end of the range, an improvement in selectivity is obtained when the feed is treated in the presence of an amount of water of the order of 0.5 mole of water per mole of feed. Comparative trials have also shown that it is preferable to maintain a molar ratio of water/feed which does not exceed about 5. This upper limit varies according to the composition of the feed. Thus the molar ratio of water/feed is preferably lower than about 1.5 when the feed is formed of a mixture of propane and propylene containing about 10% by weight of propylene. Generally, the amount of water to be used is such that the molar ratio of water/feed is from 0.5 to 1, but it may however be higher when the feed has a high propylene content. 50 55 60
- The process of the present invention is very flexible and it may be carried out in the gaseous and/or in the liquid phase. Reaction temperatures are generally from 300 to 550°C. Tempera- 65 65

tures lower than 300°C only give very low yields, while temperatures higher than 550°C cause some degradation of the reaction products. Generally, temperatures from 300 to 500°C and more particularly from 320 to 475°C will be used. Temperature variations within these limits practically do not modify the distribution of the products formed.

- 5 The hourly space velocity of the reaction mixture, expressed as the weight of said mixture per hour and per weight of catalyst (WHSV), may vary from 5 to 100. Typically, it depends on the composition of the feed. Also, a high space velocity allows for a better isobutene selectivity to the detriment of the conversion rate of the feed. 5

- 10 Whenever the feed essentially consists of propylene, the WHSV used is preferably from 75 to 125, whereas when the feed contains about 10% propylene, the WHSV is preferably from 25 to 80. 10

The pressure at which the reaction is to be carried out may vary over a rather wide range, e.g. ranging from sub-atmospheric pressure to an absolute pressure of 50 bars, typically from 0.5 to 20 bars. It is advantageous to work at low pressures to favour the production of isobutene.

- 15 A man skilled in the art should readily be able to determine, within the above-mentioned ranges, the operating conditions which will give the best yields as a function not only of the composition of the feed but also of the desired results. Thus, certain conditions, like a high WHSV, favour the formation of isobutene with a low conversion rate of the feed; under such conditions, it is advantageous to recover the isobutene from the reaction products, then to recycle the isobutene-free reaction products to submit them to a new treatment along with fresh feed. 15 20

The following Examples are given to illustrate, but not limit, the present invention.

#### Example 1

- 25 Propylene and steam were passed together over silicalite at 397°C, at a pressure of 1 bar, with a molar ratio water/feed of 0.75 and a WHSV of 93.2. 25  
51.1% of the propylene was converted, and the selectivity in isobutylene was 18.68%.

#### Example 2

- 30 Propylene and steam were passed together over silicalite at 309°C, at a pressure of 0.8 bar, with a molar ratio water/feed of 0.72 and a WHSV of 97.2. 30

The reaction products had the following composition:

- |    |                                |                                 |    |
|----|--------------------------------|---------------------------------|----|
|    | C <sub>1</sub> -C <sub>2</sub> | 1.4% by weight                  |    |
| 35 | propylene                      | 36.3                            | 35 |
|    | propane                        | 1.0                             |    |
|    | all butenes                    | 29.6 (including isobutene 12.2) |    |
|    | butanes                        | 1.2                             |    |
| 40 | C <sub>5</sub> +               | 30.5                            | 40 |

Thus the isobutene selectivity was 19.19 weight %.

#### Example 3

- 45 A feed, containing 71.07 wt% of propylene and 28.93 wt% of propane, was passed together with steam over silicalite at a temperature of 350°C, at a pressure of 14 bars, with a molar ratio water/feed of 0.92 and a WHSV of 76.6. 45

The conversion rate of propane was 11.3 wt% and that of propylene was 81.7 wt%. The isobutene selectivity was 12.63%.

- 50 Example 4 50

A feed, containing 89.31 wt% of propane and 10.69 wt% of propylene, was passed together with steam over silicalite at a temperature of 349°C, at a pressure of 15 bars, with a molar ratio water/feed of 0.88 and a WHSV of 73.2.

- 55 8.3% by weight of the propane and 70.7% by weight of the propylene were converted. The isobutene selectivity was 14.46%. 55

#### Example 5

Propylene was passed together with steam over silicalite at a temperature of 301°C, at atmospheric pressure, with a molar ratio water/feed of 0.82 and a WHSV of 5.2.

- 60 The conversion rate of propylene was 93.8% and the isobutene selectivity was 10.27%. 60  
For comparative purposes, the same experiment was repeated, in the absence of steam. The isobutene selectivity was only 6.93%.

#### Example 6

- 65 A feed, containing 71 wt% of propylene and 29 wt% of propane, was passed together with 65

steam over silicalite at a temperature of 400°C, at a pressure of 14.7 bars, with a molar ratio water/feed of 2.62 and a WHSV of 32.8.

13.4 wt% of the propane and 80.1 wt% of the propylene were converted, and the isobutene selectivity was 13.14%.

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#### Example 7

Propylene was passed together with steam over silicalite at a temperature of 301°C, at atmospheric pressure, with a molar ratio water/feed of 1.64 and a WHSV of 5.26.

90.4 wt% of the propylene was converted and the isobutene selectivity was 10.95%.

10 For comparative purposes, the same feed was passed without water vapour over silicalite at a temperature of 300°C, at atmospheric pressure and at a WHSV of 5.24. The isobutene selectivity was only 5.91% and the conversion rate of propylene was 95.0%.

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#### Example 8

15 Propylene was passed together with steam over silicalite at a temperature of 310°C, at a pressure of 0.8 bar, with a molar ratio water/feed of 0.72 and a WHSV of 97.1.

After 10 hours, the conversion rate of the propylene was 63.7% and the isobutene selectivity was 19.19%.

20 For comparative purposes, the same propylene feed was passed in the absence of steam over silicalite at a temperature of 310°C, at a pressure of 0.8 bar and at a WHSV of 95.8. After 10 hours, the conversion rate of the propylene was 58.2% and the isobutene selectivity was only 4.1%.

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#### CLAIMS

25 1. Process for producing isobutene which process comprises contacting a propylene containing feed with a catalyst consisting of a crystalline silica polymorph of the silicalite type, in the presence of steam, the molar ratio of water:feed being from 0.5 to 5.

2. Process according to Claim 1, wherein the molar ratio of water:feed is from 0.5 to 1.

30 3. Process according to Claim 1 or 2, wherein the reaction is carried out at a temperature of from 300°C to 550°C.

4. Process according to Claim 3, wherein the reaction is carried out at a temperature of from 300 to 500°C.

5. Process according to Claim 4, wherein the reaction is carried out at a temperature of from 320 to 475°C.

35 6. Process according to any preceding Claims, wherein the amount of reaction mixture treated expressed in weight per hour per weight of catalyst (WHSV) is from 5 to 150.

7. Process according to Claim 6, wherein the reaction is carried out at a WHSV of from 25 to 125.

40 8. Process according to any one of the preceding Claims, wherein the reaction is carried out at an absolute pressure ranging from a sub-atmospheric pressure to 50 bars.

9. Process according to Claim 8, wherein the reaction is carried out at a pressure of from 0.5 to 20 bars.

10. Process according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 8.

45 11. Isobutene whenever prepared by a process as claimed in any one of the preceding claims.

50 12. Process for converting a propylene-containing feed in the presence of a catalyst consisting of crystalline polymorph silica of the silicalite type, which process comprises carrying out the conversion in the presence of steam, at a molar ratio of water:feed of from 0.5 to 5, to produce a mixture containing isobutene.

13. Process according to Claim 12, wherein the molar ratio of water:feed is from 0.5 to 1.

14. Process according to Claim 12 or 13, wherein the reaction is carried out at a temperature of from 300 to 550°C.

55 15. Process according to Claim 14, wherein the reaction is carried out at a temperature of from 300 to 500°C.

16. Process according to Claim 15, wherein the reaction is carried out at a temperature of from 320 to 475°C.

17. Process according to any one of Claims 12 to 16, wherein the amount of reaction mixture treated expressed in weight per hour per weight of catalyst (WHSV) is from 5 to 150.

60 18. Process according to Claim 17, wherein the reaction is carried out at a WHSV of from 25 to 125.

19. Process according to any of Claims 12 to 18, wherein the reaction is carried out at an absolute pressure ranging from a sub-atmospheric pressure to 50 bars.

65 20. Process according to Claim 19, wherein the reaction is carried out at a pressure of from 0.5 to 20 bars.

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21. Process according to Claim 12 substantially as hereinbefore described in any one of Examples 1 to 8.

22. Isobutene-containing mixtures whenever obtained by a process as claimed in any one of Claims 12 to 21.

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